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IN SEDIMENTARY ROCKS

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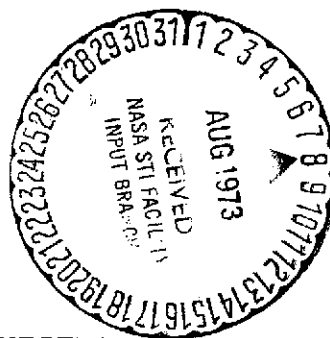
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# ORGANIC GEOCHEMISTRY OF AMINO ACIDS IN SEDIMENTARY ROCKS

Masahiko Akiyama\*

It is a known fact that organic substances are preserved in 120\*\* sedimentary rocks. They are most typically preserved in the forms of petroleum and coal. Concomitant with progress in the studies of organic substances in sedimentary rocks, numerous organic substances were discovered recently in various ages and types of rocks. Even if those found in petroleum are excluded, more than 500 kinds have been found. Degens (1967) classified these organic compounds as follows:

- 1) Amino acids and the related substances
- 2) Carbohydrates and their derivatives
- 3) Lipids, isoprenoids, and steroids
- 4) Heterocyclic compounds
- 5) Phenols, quinones and their related substances
- 6) Hydrocarbons
- 7) Asphalt and other similar substances

Above is the organic chemical classification. In some cases it is more meaningful to classify by the diagenetic processes as follows:

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\*\*Numbers in the margin indicate pagination of original foreign text.

- 1) Residual substances that have not undergone diagenesis
- 2) Products of diagenesis.

Hunt (1962) estimated the amount of organic substances contained in sedimentary rocks. He calculated the amount by analyzing 1000 samples from 200 strata of the world's 60 main sedimentary basins. The amounts are 2.1% in shales, 0.29% in carbonates, and 0.05% in sandstones. The total organic substances in the world amounts to  $3.8 \cdot 10^{15}$  tons. Estimating the coal deposits at  $6 \cdot 10^{12}$  tons and that of petroleum at  $0.2 \cdot 10^{12}$  tons, they only amount to 1/500, 1/16,000, respectively of the total organic substances.

As indicated above, organic substances are concentrated in shales. The total organic substances in the shales are believed to amount to  $3.6 \cdot 10^{15}$  tons. Nevertheless, the amounts of organic substances in the present sea sediments are 1.8% in shells, 2.2% in carbonaceous rocks, and 2.0% in clays. Organic substances are easily preserved in mud sediments.

As shown in Figure 1, in the composition of organic substances in the world sediments, amino acids excel among the calcic substances. In the mud sediments, humic acid and kerogen that are insoluble in organic solvents are abundant. The present status and topics of the studies relating to proteins and amino acids contained in fossils have been published (Akiyama, 1971). The significance and treatment of amino acids in sedimentary rocks differ from those in fossils. In this paper, organic geochemical consideration will be given to amino acids in sedimentary rocks.

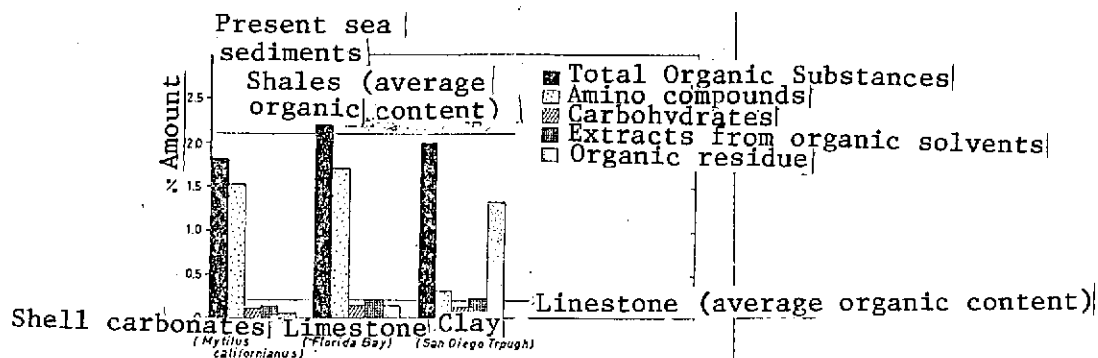


Figure 1. Compositions of main organic substances in the world sediments (Degens, 1967).

## II. Preservation of Amino Acids and Geological Age

In studying amino acids in sedimentary rocks, it is necessary to have a knowledge of the transformation of proteins and amino acids in the diagenetic process. Degens (1967) describes the transformation of organic substances in the diagenetic process as follows:

- 1) Decomposition due to bacteria and chemical reactions
- 2) Condensation of products of metabolism and hydrolysis
- 3) Slow inorganic maturing
- 4) Thermal decomposition.

Several studies are known on the changes of amino acids by tracing the same fossil type or the related type back through the geological ages. (Abelson, 1955; Akiyama, 1965; 1971; Akiyama and Wyckoff, 1970; Florkin, et al., 1961; Horita, Susumu, 1965; Horita, Nobuko, 1967; Jope, 1967; Matter, et al., 1969). /121  
One example of the changes is shown in Table 1. As is evident from the table, the total amino acid content in scallop shells decreases with age. Proteins, peptides, and amino acids decrease drastically in the Pleistocene, Pliocene, and Miocene epochs.

TABLE 1  
AMINO ACIDS CONTAINED ( $\mu\text{g/g}$ ) IN SCALLOP SHELLS OF VARIOUS  
GEOLOGICAL AGES (AKIYAMA, 1971)

	Insoluble Proteins	Soluble Proteins	Free Amino Acids	Total Amino Acids	Residual Rate to the Present Shells
Pleistocene Epoch	29.9	238.1	197.3	465.3	21.3
Pliocene Epoch	9.7	180.8	146.2	270.2	12.4
Miocene Epoch	24.9	28.8	150.7	204.5	9.4
Eocene Epoch	11.4	6.9	35.7	54.0	2.5
Cretaceous Epoch	7.6	4.1	10.6	22.3	1.0
Jurassic Epoch	4.4	5.2	7.3	16.9	0.8

Thus, proteins in fossils hydrolyze successively via low molecular peptides to amino acids (Akiyama, 1971). Since most of the organic substances in a hard substance are proteins with a minute amount of mucopolysaccharides, organic acids and lipids, decomposition is the main problem in diagenesis. In the case of sedimentary rocks, however, unlike the fossils, the main difference is that condensation reactions must be considered together with decomposition.

Rittenberg, et al. (1963) examined the amino acid content in the 170 m core of the Experimental Mohole from offshore California sediments. According to the results, the values decrease from 355.2  $\mu\text{g/g}$  at the ocean bottom to 116.3 at 1.5 meters depth, and 15.5  $\mu\text{g/g}$  at 170 meters (Figure 2).

The lowest core is said to be that of the Miocene epoch. Ichihara and Minoshi (1969) conducted an amino acid analysis of the Cenozoic era around Osaka and Boso Peninsulas. The contents are 10 — 20  $\mu\text{g/g}$  and 5 — 15  $\mu\text{g/g}$  for the Pliocene and Miocene eras, respectively. According to the information uncovered by us recently, amino acids in the Cretaceous Pierre shale of

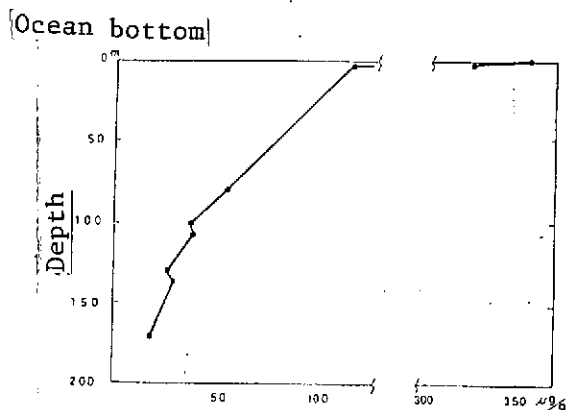


Figure 2. Distribution of amino acids in sediments of Experimental Mohole (Rittenberg, et al., 1967).

Wyoming, North America, range from 15.07 — 3.80  $\mu\text{m}/100\text{ g}$ . (Akiyama and Johns, 1972).

Excellent studies have been made by Degens, et al. (1961, 1963), on the change of amino acid composition by the sedimentation environment. They chose the sediments in San Diego Trough as those formed in an oxidizing environment, and those in Santa Barbara

Basin — in a reducing environment. As a result, they discovered that there is a close resemblance between the amino acid composition on the sediment surface of the latter, and the amino acid composition of plankton in the sea above. They concluded that in a reducing environment the amino acids in sediments originated from plankton. On the other hand, in the oxidizing San Diego Trough, the composition is determined by the organisms in the sediments (*de novo* generation). Thus, it is a significant discovery that the formation of sediments is strongly dependent on whether the environmental condition is oxidizing or reducing.

In the oxidizing San Diego Trough, total amino acids decrease with depth. The change is abrupt at the beginning, but decreases later (Figure 3). The amount of individual amino acid fluctuates considerably in sediments shallower than 4 meters. In the reducing Santa Barbara Basin, the amount of individual amino acid fluctuates around 500  $\mu\text{g}/\text{g}$ . The peak depends on the amino acid (Figure 4). Degens et al. (1961), incorporated the chromatographic separation technique by Nagy and Stevenson (1960), and explained the cause as the exclusion of occluded

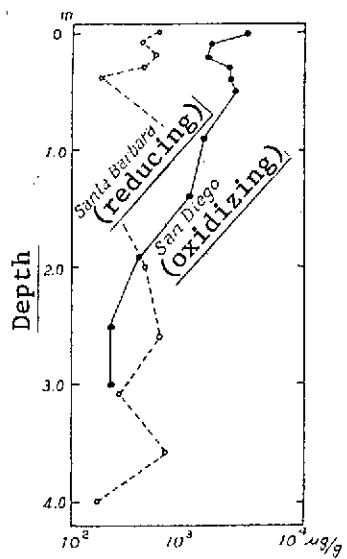


Figure 3. Comparison of amino acids in reducing (Santa Barbara Basin) and oxidizing (San Diego Trough) environments (Degens, et al., 1963).

water by pressure in which the mud acts as the stationary phase. However, as discussed later, the main amino acids in sedimentary rocks originated from kerogen,

and represent the composition at the time of deposition. Therefore, we cannot agree with the theory of Degens, et al.

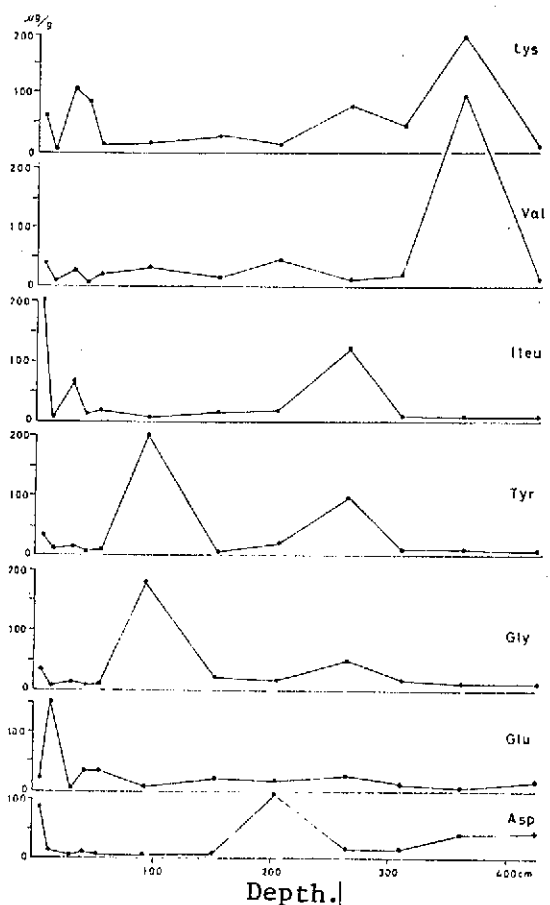


Figure 4. Depth distributions of amino acids. Chromatographic separation is occurring in sediments (Degens, et al., 1961).

In the studies of amino acids, the total amino acids is mostly discussed, since samples are normally hydrolyzed directly in hydrochloric acid. Obviously, the free amino acids must be analyzed separately from those derived from proteins and other condensed organic compounds. In the San Diego Trough studies (Degens, et al., 1965, 1964), there were no free amino

acids — most were tied in some kind of form. In this study, however, it was not clear how they were tied — that is, whether they were formed from proteins or humic acid and kerogen that had been formed by diagenesis. This is discussed later.

On the other hand, most of the sediments on the surface (0 — 10 cm) of the reducing Santa Barbara Basin contain free amino acids (Degens, et al., 1961). The table (Table 2) by Degens (1967) is helpful in finding how many amino acids are contained in the sediments of recent and various eras.

### III. Change of Amino Acids in Sediments

The interaction of bacteria with amino acids immediately after sedimentation is extremely large, and the diagenesis process cannot be discussed without its consideration.

In reducing conditions, however, the bacterial actions are considered to be very small. Table 3 shows the distribution of bacteria in Aransas Bay, Texas (Oppenheimer, 1960). As is evident from the table, even in oxidizing conditions, the bacterial activities decrease rapidly when covered with sediments. According to the studies conducted on the numerous fresh water lakes in the Soviet Union, the number of bacteria is not sufficient to decompose organic substances at depths less than 1 meter (Kuznetzoff, et al., 1965). Even in oxidizing conditions, it changes gradually to reducing conditions as the sediments deposit.

Aside from the decomposition effect, the contribution of bacteria to the composition of organic substances arises from bacteria themselves. Assuming the average size of bacteria as  $1 \cdot 2 \mu$ , and since the mass is  $10^{-11}$  g and  $10^8$  bacteria amounts to 1.0 mg/g, it is 0.1% contribution (Oppenheimer, 1960).



TABLE 2  
AMINO ACIDS IN VARIOUS SEDIMENTS (DEGENS, 1967)

	Substances	Geological Ages	Concentrations ( $\mu\text{g/g}$ )
Organic Matters	Humic Acid (5)	Present	20,000
	Peat (2)	Present	10,000
	Lignite (19)	Miocene	300
	Kerogen (3)	Pennsylvania	200
	Anthracite (3)	Jurassic-Cretaceous	1
	Petroleum (4)	Paleozoic	0.5
Carbonates	Shell (10)	Present	10,000
	Sea Limestone (4)	Present	10,000
	Shell (1)	Pleistocene	300
	Shell (1)	Miocene	50
	Sea Limestone (4)	Miocene	20
	Fresh Water Concretion (3)	Miocene	5
	Sea Limestone (2)	Pennsylvania	5
Various Sediments	Soil (6)	Present	10,000
	Sea Bottom Mud (5)	Present	5,000
	Sea Bottom Mud (2)	Pleistocene	1,000
	Sea Shale (5)	Miocene-Cretaceous	400
	Sea Shale (5)	Pennsylvania	20
	Chart (2)	Pre-Cambrian	10
	Manganese Mass	Present	5
Natural Water	Oil Field Water (15)	Paleozoic	0.20
	Sea Water (10)	Present	0.05
	Rain Water (1)	Present	0.0005
Meteorite	Carbonaceous Condrite (8)		100 (Bound) 30 (Free)
	Condrite (8)		20 (Bound) 10 (Free)

TABLE 3  
BACTERIA IN SEDIMENTS IN ARANAS BAY, TEXAS (OPPENHEIMER, 1960)

Depth (cm)	Aerobic Bacteria	Starch Dihiscent Bacteria	Anaerobic	Sulfur Reducing Bacteria
1	5,000,000	5,000,000	5,000	1,000
40	10,000	5,000,000	1,000	0
75	5,000	500	1,000	0

Krane (Jones and Vallentyne, 1960) examined the compositional variation of organic matter by adding aerobic and anaerobic bacteria to the fresh water animal plankton. As a result, they found no variation in the amino acid composition.

$\beta$ -alamine,  $\gamma$ -aminolactic acid and ornithine are detected in sediments. They were formed by the diagenesis of amino acids from proteins. This process is confirmed by the heating experiment of amino acids (Vallentyne, 1964). The change of amino acids to other amino acids by heat treating is summarized in Table 4.

Thermal decompositions of amino acids are examined by heating the aqueous solution (Abelson, 1959; Vallentyne, 1968) or the mixture of calcium carbonate powder (Jones and Vallentyne, 1960; Vallentyne, 1964). Three changes are known by the decomposition. The change of one amino acid to the other is brought about by the side chain reaction (R). The others are deamination and decarboxylation. Organic acids are formed from the former, and amine from the latter. The selectivity of the reaction with experimental conditions, however, is not known. The stabilities of many amino acids are plotted by Vallentyne (1965) (Figure 5).

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TABLE 4  
AMINO ACIDS FORMED BY HEAT TREATMENT

Original Amino Acids	Formed Amino Acids
Serine	Glycine•Alanine
Threonine	Glycine•α-Aminolactic Acid
Valine	Glycine
Cysteine	Alanine
Cystine	Alanine
Methionine	Glycine•Alanine•α-Aminolactic Acid
Tyrosine	Glycine
Histidine	Glycine•Alanine
Aspartic Acid	β-Alanine
Glutamic Acid	γ-Aminolactic Acid
Arginine	Orithine

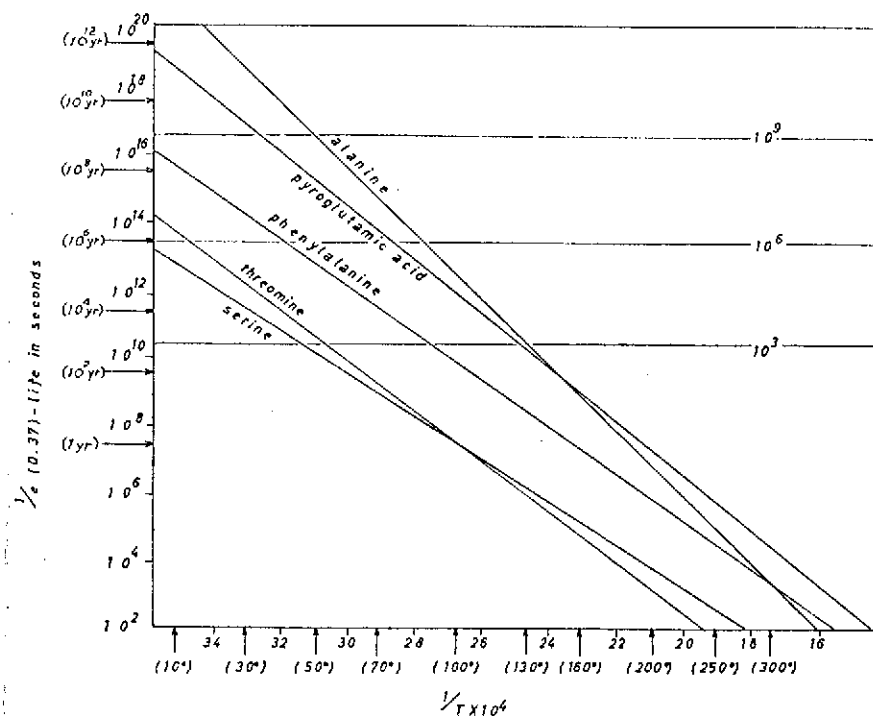


Figure 5. Thermal decomposition of five amino acids (0.01 M solution) (Vallentyne, 1965).

TABLE 5  
STABILITIES OF AMINO ACIDS (ABELSON, 1954)

Relatively stable	Alanine, glycine, glutamic acid, leucine, isoleucine, proline, valine, E~44,000 cal/mole
Rather stable	Aspartic acid, lysine phenylalanine
Relatively unstable	Serine, threonine, arginine, tyrosine

Decarboxylation occurs by heating alanine, which can be represented as a first order reaction as,

$$dC/dt = -kC$$

where C is the alanine concentration, k is  $k = Ae^{-E/RT}$  where A is the frequency factor, E is the activation energy, R is the gas constant, and T is the absolute temperature. In the case of alanine,  $k = 3 \cdot 10^{13} e^{-44,000/RT}$ . Therefore, it can survive a few hours at 250° C, 1000 years at 120° C, and 10 billion years at ambient temperature.

Abelson separated amino acids into three classes according to their stabilities (Table 5). This was established by the stability experiment conducted in an aqueous solution. A similar result is obtained with the calcium carbonate method (Jones and Vallentyne, 1960). The stability is said to be different in the presence of clayey minerals (Proshnowsky and Schidlowski, 1967). The proteins in shells contain parts that are not decomposable by heating to 800° C (Gregoire and Voss-Foucart, 1970).

In the heating experiments, pH cannot be neglected aside from the temperature factor. The effect of pH depends on the amino acid. Table 6 shows the changes occurring by heating at 140° C for four days (Hare and Mitterer, 1969).

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TABLE 6  
CHANGE OF AMINO ACIDS BY HEATING AT VARIOUS pH  
(HARE AND MITTERER, 1969)

Amino Acid \ pH	9.4	4.6	20
Arginine	Ornithine	No Change	No Change
Cystine	Unstable	Unstable	Stable
Alloisoleucine	0.2	—	0.05
Aspartic Acid	Stable	Unstable	Stable
Serine, Threonine	10	1.5	0.3

When deamination and decarboxylation occur simultaneously, hydrocarbons are formed. Most of the hydrocarbons range from  $C_1$  —  $C_5$  (Table 7). Thompson and Creath (1966) deduced the gradual change of amino acids to hydrocarbons from the analyses of many fossil shells.

Data on the thermal decomposition occurring outdoors are extremely limited. Degens (1965, 1968) conducted the analysis of amino acids in the Cretaceous Pierre shale in North America where there is a 1 meter basic lava bed. He analyzed the shales 15 cm, 60 cm, 250 cm, and 430 cm from the lava and found 0.76, 0.75, 4.39  $\mu\text{M}/100$  g amino acids, respectively. The amino acid content in the unchanged Pierre shale ranges from 3.83 — 15.07  $\mu\text{M}/100$  g (Akiyama and Johns, 1971). Hence, the above four values indicate the changes by heating due to the penetration of the rock bed. Thus, the amino acid content decreases rapidly as the lava bed is approached, but the composition hardly changes (Degens, 1965).

Let us now consider the optical activity of amino acids. All amino acids except glycine have optical isomers because of the asymmetric  $\alpha$ -carbon. However, the hydrolysates from the proteins of living matter are all L-amino acids.

TABLE 7  
HYDROCARBONS FORMED FROM AMINO ACIDS  
(THOMPSON AND CREATH, 1966)

Methane	Glycine, argenine, histidine, methionine
Ethane	Alanine, aspartic acid, serine, cystine
Propane	$\alpha$ -amino lactic acid, glutamic acid, threonine, methionine
i-Butane	Valine
n-Butane	Ornithine, argenine, histidine, proline
i-Pentane	Leucine, isoleucine
n-Pentane	ricin

Amino acids remaining in fossils have been racemized. It is not difficult to deduce that in the process of passing through the geological ages, they change into racemates. Hare and Abelson (1968) confirmed the racemization using L-amino acid oxidase enzyme. It is evident from the result shown in Table 8 that racemization is completed in the Miocene fossils. Alloisoleucine forms as a product of racemization from isoleucine. From the in-situ experiments, the ratio (allo-Ileu/Ileu) is 1.25. The values for the amino acids in fossils are 0.32 for the upper Pleistocene period and 1.25 for the Miocene period indicating that the equilibrium is attained (Hare and Mitterer, 1969).

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On the racemization of amino acids in sediments, Kvenvolden (1969) succeeded in the separation of D, L-amino acid by the gas chromatograph method using a capillary column. The samples were taken from the 34.8 meter core at Saanich Bay in British Columbia. According to the results, although there is a difference depending on the amino acid, D-amino acid increases with depth; at the deepest part 1 — 10% D-amino acid is formed. The age is estimated at 9000 B.P. at 34.5 — 34.8 meter core.

TABLE 8  
RACEMIZATION OF AMINO ACIDS IN MERCENARIA SHELL  
(HARE AND ABELSON, 1968)

	'Present Total Weight	Late Pleistocene Total Weight	Late Pleistocene Soluble Fraction	Miocene Total Weight
Glutamic Acid	< 5	22	11	47
Proline	0	31	19	52
Alanine	0	40	10	51
Valine	0	28	5	52
Alliosoleucine	—	98	100	95
Isoleucine	0	0	0	< 5
Leucine	0	26	5	48
Tyrosine	0	25	16	50
Phenylalanine	0	25	8	49

Based on the above age, the half life of L-amino acid, hence, is 25,000 — 220,000 and requires  $3 \cdot 10^5$  —  $2 \cdot 10^6$  years for the complete racemization. Also, the effect of pH on the racemization cannot be neglected; the racemization of  $\alpha$ -alanine and  $\alpha$ -glutamic acid is accelerated in a weakly alkaline condition. Abelson and Hare (1969) point out the possibility of contamination in the present age based on the fact that all amino acids in Gunflint chert are L-type.

#### IV. Condensation of Amino Acids

In soils or young sediments, there is an organic compound called humic acid that is extracted with base and precipitated with acid. More than 50% of the organic compounds in the unsolidified sediments is humic acid.

Amino acid is extracted when kerogen or humic acid are hydrolyzed with hydrochloric acid. The composition of amino acids is similar to kerogen and humic acid (Degens, 1968). According to Degens and Hunt (1964), 357  $\mu$ M/g amino acids are

obtained when the humic acid from San Diego Trough is heated in 6N hydrochloric acid. Heating under the same conditions for five days yielded only 32.2  $\mu\text{M/g}$ . Amino acids extracted under such severe conditions are those that had been incorporated in the humic acid structure. There are other amino acids that are easily extractable; these probably had been absorbed by humic acid.

From such facts, amino acids in sedimentary rocks are considered to have been incorporated in the structures or absorbed in kerogen and humic acid. In order to clarify this problem, it is necessary to graduate the amino acids in sedimentary rocks and trace their origins.

We (Akiyama and Johns, 1972) had the opportunity to study /127 organic matter in the Cretaceous Pierre shale in Wyoming, North America. As mentioned previously, 3.83 — 15.07  $\mu\text{M}/100\text{ g}$  amino acids are contained in the Pierre shale. There are three possibilities: (1) Free amino acids; (2) Amino acids from kerogen; (3) Amino acids between the layers of clayey minerals. Amino acids from proteins, also, must be considered. Proteins belong to category (2), but even if they are present, they are in a negligible quantity. As a result of the analytical procedure shown in Figure 6, amino acids belonging to (2) occupy 60 — 80% of the total. It can be deduced that at least the amino acids in the Pierre shale come from kerogen.

It becomes necessary, then, to clarify the contribution of amino acids toward the formation of kerogen in studying the amino acids in sedimentary rocks. Recently, Abelson and Hare (1971) disclosed how kerogen selectively surrounds amino acids in the seven samples of sea and land deposited sediments including those from the Black Sea. The selectivities are in the



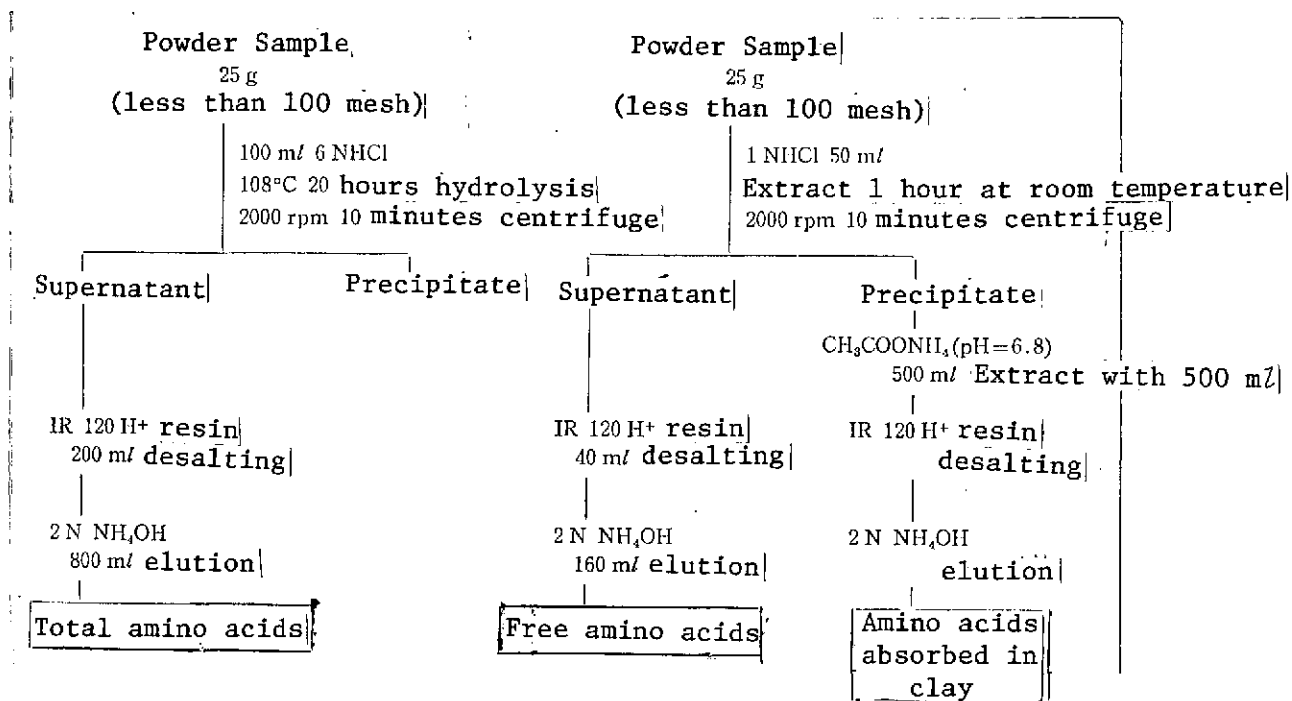


Figure 6. Extraction procedures of amino acids in sedimentary rocks.

order of: (1) cystine; (2) basic amino acids; (3) tyrosine, phenylalanine. It was found that the absorption of amino acids decreases when kerogen is reduced, and increases when it is oxidized. By reacting glucose with amino acids, they synthesized kerogen and humic acid, and found that they exhibit the same absorption characteristics as the natural ones. In the reaction of glucose and phenylalanine, 25% is reacted in a day, but the maximum yield does not exceed 60%, no matter how long they are reacted. The formation of kerogen is fast with glucose and ricin, but does not form with alanine. The reaction rate of humic acid is slow; the yield is only 20% after six months. From the above experiments, it became clear that amino acids play a role in the formation of humic acid and kerogen. Also, it is seen that kerogen is formed via humic acid which is formed by the condensation reaction of amino acids and carbohydrates.

Abelson (1967) showed that hydrocarbons are formed by the heat treatment of kerogen. The Eocene Green River shales are rich in organic matter and contain as much as 34%. By heating these organic matter at various temperatures below 200° C, hydrocarbons comprised mostly of isobutane and isopentane at low temperatures, and mostly methane at high temperatures, are formed. The former arises from the decomposition of amino acids, and the latter from kerogen.

It has already been seen that amino acids formed by the hydrolysis of proteins change to hydrocarbons by heating. Kerogen formed from amino acids by the condensation reaction change back to hydrocarbons by the subsequent diagenesis process.

#### V. Oldest Amino Acids

There have been many reports concerning the detection of amino acids in the Pre-Cambrian fossils. Abelson and Hare (1968) analyzed the amino acids in the Gunflint chert, and concluded that they are the contaminants of the present age. Although there are the analytic values of Schoff, et al. (1968), for the amino acids in the Gunflint chert, the values of Abelson and Hare are much smaller, and the detected amino acids are digested by L-amino acid oxidase enzymes. If they were the amino acids of the Pre-Cambrian Age, they would indicate the complete racemization by the diagenesis process.

From the Fig Tree System ( $3.1 \cdot 10^9$  years) distributed in the East Transvaal district of Africa, Kvenvolden (1969) detected n-alkane, isoprenoid together with glycine, alanine as free amino acids, and glycine, serine, threonine, leucine, alanine, valine, proline, aspartic acid, glutamic acid,  $\beta$ -alanine, phenylalanine, and isoleucine as bound amino acids. The content

is calculated as 2nM/g. They showed by a gas chromatograph equipped with capillary columns that the amino acids are the L(+) type. Their conclusion is different from that of Abelson et al.: that is, the above amino acids were originally contained in the rocks for other reasons, and the fact that they are the L-type amino acids indicates that biological activities were vigorous already three billion years ago. The bound amino acids have not been examined, but the possibility of having a kerogen origin is high.

Undoubtedly, as mentioned by Abelson and Hare (1968), the free amino acids have completely racemized in the Miocene era which is different with the bound amino acids. For the proteins in shell fossils, the formation of alloisoleucine has hardly proceeded (Akiyama, 1971; Akiyama and Johns, 1972). Hence, it is probably premature to conclude that they are the contaminants of the present age just from the reason that the amino acids in the Pre-Cambrian rocks have not racemized.

## VI. Early Environment and Amino Acid Composition

There are very few studies on the deduction of the early environment from the composition of organic matter in sedimentary rocks. Since there is a compositional difference between fatty acids in land plants and sea organisms, by examining the composition of fatty acids in sedimentary rock it is possible to distinguish between the land deposit and the sea deposit (Fan, 1971). There are studies relating the environment to the composition of hydrocarbons. That is, in the photosynthesized organisms there are many light hydrocarbons, whereas there are many heavy hydrocarbons in the others (Han<sup>f</sup>, et al., 1968). Based on this fact, it has been concluded that the organic deposits (5000 years old) in the Mud Lake of Florida are due to non-photosynthesized organisms (Calvin, 1970).

Ho (1966) studied the proteins contained in fresh water shells of various eras from the Pleiocene to the present, and derived the factors determining the decomposition rates of proteins. He mentions that the water content is the major factor in a dry climate. He deduced the dry climate from the comparison of the amount of residue of proteins in the Pleistocene shells and the slow decomposition rate during the Illinois — early Wisconsin Periods. The inference agrees well with other geological data.

There are only few studies made on the relationship between the deposition environment and the amino acids in deposits. There is no example of the attempt to deduce the early environment from the amino acids in the sedimentary rocks of early geological periods. We attempted correlation studies of the early environment with the amino acids in the Pierre shale of Wyoming, North America (Akiyama and Johns, 1971).

We chose two sections — one is Salt Creek and the other Red Bird (Figure 7). In the Salt Creek section, the amino acid content reached the maximum in the uppermost non-sea-deposited layer (Lance layer) and decreased steadily to the lower layers. There is a peak in the middle non-sea-deposited layer (Parkman Sandstone). The fluctuation in the amino acid content shows a correlation with the deposition environment. The supply of organic matter from land corresponds with the high content. The factors determining the content of organic substances are: (1) The amount of organic matter supplied at the time of deposition; (2) Deposition rate; (3) Storage condition. In general, one cannot infer the early environment from the amount of amino acids in the deposit. At least with the Pierre Shale, (1) is the important factor.

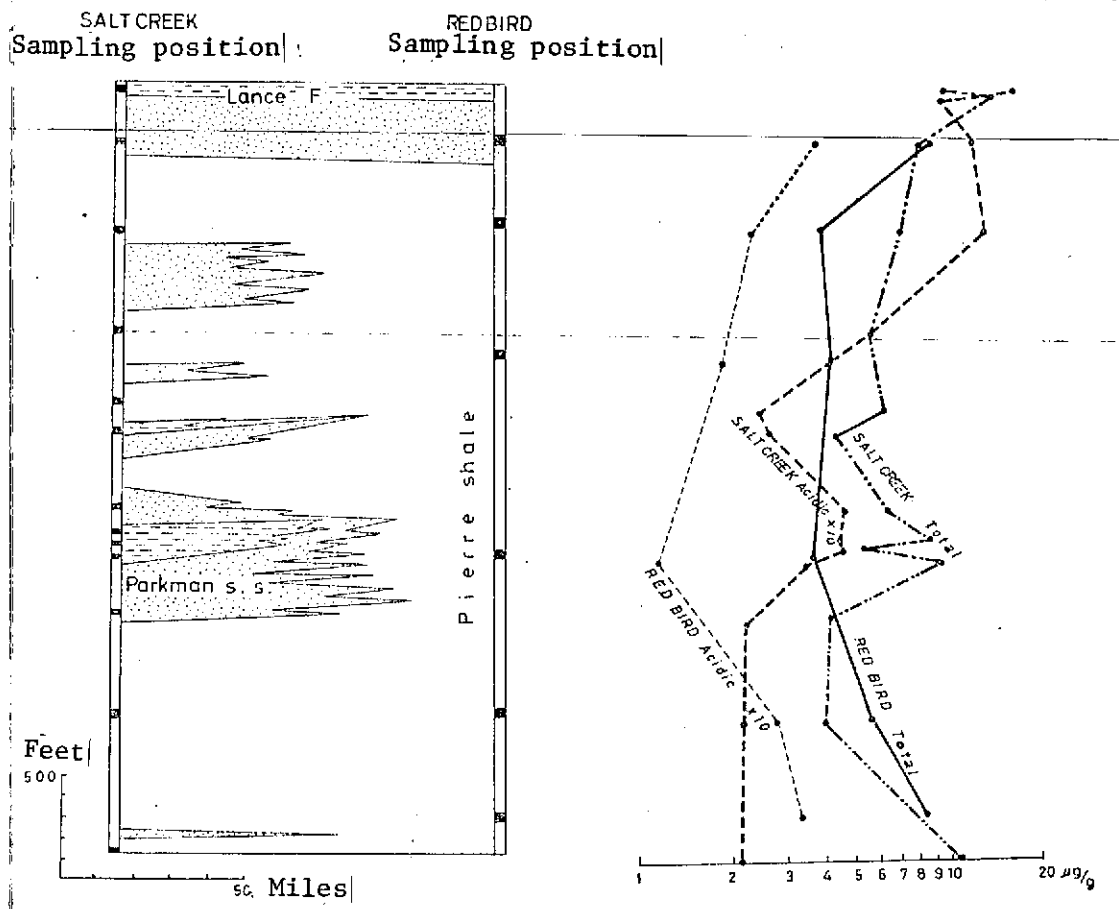


Figure 7. The phase change and amino acids in Pierre Shale, Wyoming: broken line, non-sea-deposited layer; dot, sea formed sandstone; blank, shale.

If we classify the 19 amino acids in the Pierre shale into neutral, basic, acidic and cyclic groups and examine the relationship between the composition and deposition environment, except for the acidic amino acid group, the remaining three groups are in parallel relationship with the change in the total amount. There is no characteristic difference with the acidic amino acids in the Red Bird section where all the entire layers are composed of an offshore type deposit. At Salt Creek, where the deposition environment abounds in changes, there is a difference in the amino acids between each layer. That is, the

relative amount of acidic amino acids is high in the non-sea-deposited layer and the shore-deposited layer, and low in the offshore deposited layer (Figure 7).

Amino acids in the sediments of oxidizing San Diego Trough originated from organisms living in the area (*de novo* generation), and from planktons in the reducing Santa Barbara Basin. Under these two different environments there is a big difference in the acidic amino acid concentration in sediments. In the reducing environment, it measures 14% of the total, whereas in the oxidizing environment none is detected. Degens (1964) extracted humic acid from sediments on the bottom (0 — 0.2 m) of San Diego Trough and analyzed for the amino acids in the hydrolysates. Amino acids in humic acid reached 10% of the total. The acidic amino acids occupied 20.9%, that is, only 0.7% of the total amino acids in sediments. The value of  $\delta^{13}\text{C}$  in humic acid is -21.8 indicating it is clearly of land formed origin. However, there is a problem in the interpretation of the isotope ratio. That is, there is a localization in the distribution of carbon isotopes in a molecule. Since carbon in a carboxyl group abounds in  $^{13}\text{C}$ ,  $^{12}\text{C}$  in amino acids enriches by 20% as a result of decarboxylation. Hence, it can be considered that decarboxylation occurred at the time of formation of humic acid, and the value of  $\delta^{13}\text{C}$  decreased.

There are not many studies made on the amino acids in non-sea-deposited sediments. Jones and Vallentyne (1960) analysed the sediments 7 meters below the bottom of Opinicon Lake, and found that acidic amino acids amount to 18% of the total amino acids. Kleerekoper (Jones and Vallentyne, 1964) analyzed the amino acids on the bottom of the Ontario Lake and reported 18.6% acidic amino acids. From the values obtained from the sediments on the bottoms of many lakes in North America, Swain (1961)

indicates the high acidic amino acid content in neutral-alkaline lakes. At any rate, these data indicate that a large quantity of acidic amino acids is stored in the sediments on the lake bottom.

Thus, the fact that in recent sediments the acidic amino acid content is high in the lake bottom sediments supports the correlation between the acidic amino acid content in the Cambrian Pierre Shale and the ancient deposition environment. Nevertheless, it is necessary to study the relationship between the amino acid composition in the present sediments and the deposition environment.

## VII. Conclusions

I have studied the amino acids in fossils and sediments from a geochemical point of view, and attempted a systematization. The paleochemical problems of amino acids in fossils were discussed elsewhere (Akiyama, 1971).

The diagenetic process of proteins in sediments differs from that in fossils. In the former, the bacterial action is quite pronounced; especially under oxidizing conditions, that is the main decomposition factor. The second difference is that the amino acids formed by hydrolysis react with carbohydrates and form stable compounds such as humic acid and kerogen. Amino acids extracted from sedimentary rocks are those which had been stabilized and stored in kerogen. Hence, the stability study of free amino acids is not sufficient to establish the stability of amino acids in sediments.

Amino acids in sediments reflect the amino acid composition at the time of deposition; they appear to have existed in the forms of humic acid and kerogen. If it is true, a possibility arises that one can deduce the early environment at the time of sedimentation based on the amino acid composition in sedimentary rocks. Compelled by such thoughts, the study on the Pierre shale of North American Continent was pursued and presented.

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16. Abstract This paper represents a review of the amino acid distribution and of the diagenetic fates of proteins in recent and ancient sediments. The diagenetic process of the organic compounds in sediments differs from that in fossils in the following two aspects: (1) the protein in sediments is suffered by active bacterial destruction especially under oxidizing conditions and (2) the resulting hydrolysates (amino acids) are polymerized with the other organic compounds therein such as carbohydrate, lignin or fat, producing humic acid or kerogen in sediments. Most of the survival amino acids in the ancient sediments are derived from the kerogen or humic acid, which may give the similar composition to the original protein at its deposition. It is suggested that the depositional environment can be inferred from the amino acid composition in the ancient sediments.					
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